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Non-marine carbonate: wherefore art thou?

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Although notoriously difficult to delineate from the wider family of carbonate rocks and sediments, non-marine carbonates represent an important subset, forming in a large variety of depositional settings such as lakes, rivers, hydrothermal vents, caves, soils and sites affected by alkaline pollution (Pentecost, 2005; Alonso Zarza & Tanner 2010; Capezzuoli et al., 2014; Della Porta, 2015) (Figure 1). Due to the erosive and dissolution effect of meteoric waters in terrestrial environments, such carbonates are generally characterised by low preservation potential and their geological record is likely discontinuous and highly altered. Nevertheless, non-marine carbonates represent a significant component of terrestrial sedimentary basins, providing useful proxies of

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palaeoenvironmental conditions and can offer a means of passive remediation of sites harmed by human industry, including sequestration and storage of carbon dioxide. Understanding the physico-chemical and microbially mediated processes involved in their precipitation helps to constrain biogeochemical cycles, investigate the geological past and plan for the future approaches to global changes.

In the last two decades, the study of non-marine carbonates has progressed from descriptions of local occurrences to frontier research, able to envelope the very latest challenging interests such as the dawn of life on Earth or astrobiological research (including such work as Rothschild & Mancinelli, 2001; Farmer, 2000; Des Marais & Walter, 2019; Franchi & Frisia, 2020), and has become a major target for future geo-engineering research.

This special issue aims to begin to gather and curate the knowledge necessary to resolve the challenges this frontier research faces. We need better insights into the variety of non-marine carbonate facies and the physico-chemical and biogenic controls on processes of carbonate and associated minerals precipitation to move our studies beyond observation of what has happened, to reconstruct processes in time and space. The collected contributions investigate fossil and modern non-marine carbonates through multi-disciplinary approaches highlighting their variability across different depositional environments and ages and the biological, environmental and chemical factors controlling their formation, fabrics and accumulation rates.

Where do non-marine carbonates form?

In terrestrial environments, the presence of calcium bicarbonate-rich waters is extremely common and consequently so is their ability to precipitate non-marine carbonates, both in natural and in human-induced settings (such as cement waste, steel slag or bauxite refining residue "red mud" with atmospheric carbon dioxide). Accordingly, such deposits can be recovered displaying various sizes, degrees of purity and geometry in a wide spectrum of depositional and diagenetic settings, from sites where life is flourishing to the most inhospitable.

This is the case of the hypersaline Great Salt Lake (Utah – USA) that is the location of two studies presented here. Homewood et al. (2021) show the depositional record of transitional shoreline palaeoenvironments that fell from Lake Bonneville levels to low-stand Great Salt Lake levels, providing a rare example of onshore groundwater spring deposits connected to lacustrine microbial bioherms.

The study by Baskin et al. (2021) enables us to assess the distribution of actual sublittoral microbial bioherms in the Great Salt Lake by means of side scan sonar and CHIRP mapping, linked to reprocessing of acoustic data from bathymetric surveys, with significant implications for managing and protecting the lake ecosystem.

Many terrestrial sites, characterised by subaerial springs and flowing waters, represent ideal settings where calcium bicarbonate-rich waters can precipitate different structures depending on the different climate situations. This is the case of the contribution by Arenas (2021) who focusses on freshwater fluvial stromatolites and oncolites as tools to seek diverse environmental and climate information at different temporal scales.

This special issue includes examples of non-marine carbonates from African volcanic areas (Bongongo and Ngol areas, South West Cameroon) where Bisse et al. (2021) describe the sedimentology and trace element (such as REEs) concentrations of fossil and active spring deposits related to deep-seated, hydrothermal, crustal fluids in contact with volcanic rocks and the breakdown of plagioclase from the Cameroon Volcanic Line alkali basalts.

Going back through time, non-marine carbonates represent a valuable record of modern arid playa lakes from ancient Earth history, as shown by Bartley et al. (2021) from the Mesoproterozoic Rosport Formation of Ontario (Canada), where evidence of a hypersaline lake precipitating both carbonate and gypsum during periods of increased aridity and low clastic influx, was depicted.

Why do non-marine carbonates form and evolve?

One of the most pressing aspects concerning non-marine carbonates are the controls on the processes of carbonate precipitation, both physico-chemical and biogenic. Various precipitation processes control the large variety of depositional features and fabric types

produced, especially when considering their intimate interaction with microbiology. The study by Mercedes-Martin et al. (2021) highlights the roles of concentration regimes associated with biopolymers and microbial metabolism against the background salinity fluctuations in determining the morphological and textural transitions in lacustrine carbonate minerals.

In the same context, the contribution by Della Porta et al. (2021) evidences how microbial communities in subaerial hydrothermal vent settings vary as a function of water temperature and that the resulting travertine precipitation is influenced by biofilm Extracellular Polymeric Substances (EPS-mediated mineralization), affecting the fabric types, independent of specific microbial community composition and metabolism. The contribution by Rogerson et al. (2021) describes experiments on how EPS influences carbonate mineral growth, exploring the complexity of the interaction of EPS presence/absence, specific mixtures present in nature and their complex and dynamic interaction with both mineral surfaces and hydrochemical conditions.

Not to be underestimated is the fate of non-marine carbonates after deposition, due to their susceptibility to secondary diagenetic processes. The study by De Boever et al. (2021) deals with travertine deposits from Mammoth Hot Springs in Yellowstone National Park (USA), where revisiting a borehole core, drilled in 1967 at one of the upper terraces, allows the nature, impact and timing of travertine early diagenesis, fabrics and geochemical signatures to be unravelled, illustrating how these data compare with present-day hot-spring carbonates.

World geo-heritage sites encompassing non-marine carbonates

Not surprisingly, frequently spectacular non-marine carbonates are the dominant deposits of many globally renowned historic or tourist sites. The list includes sites such as Plitvice (Croatia) and its calcareous tufa, Carlsbad (USA) and most of the world caves for their speleothems, Pamukkale (Turkey) and Yellowstone (USA) for their travertine depositional systems. One of these examples is the Huanglong travertine landscape, located on the eastern edge of the Qinghai-Tibet Plateau, where Qiu et al. (2021) provide age data for

the late Cenozoic environmental events such as climate variation and continental activity on the eastern margin of the Qinghai-Tibet Plateau. Similarly, the manuscript by Scalera et al. (2021) also discusses the last evolutionary stages of another of these historical sites by means of sedimentological, petrographic and diagenetic studies. The Acque Albule Basin (Tivoli, Italy) is one of the largest hydrothermal travertine sites in the world, and a keystone in the local economy.

Emerging applications of knowledge about non-marine carbonates

In the last decade, non-marine carbonates were often the target of studies concerning research fields or applications apparently distinct from classical sedimentary geology/tectonics. For instance, great attention has been addressed to their petrophysical properties and reservoir potential in consideration of recent South Atlantic subsurface hydrocarbon discoveries (Carminatti et al., 2008). In this view, the study by Soete et al. (2021) concerns a travertine spring carbonate reservoir analogue applying petrophysical characteristics to understand plug scale porosity and permeability heterogeneities utilising an integrated methodology, including petrography, Mercury Injection Capillary Pressure, laboratory Nuclear Magnetic Resonance and X-ray Computed Tomography. Also the manuscript by Rejmer et al. (2021) aims to determine variations in petrophysical properties within a Miocene mixed alluvial to lacustrine carbonate system (Madrid Basin, Central Spain) and highlights how travertine deposits are dominated by larger Equivalent Pore Aspect ratios compared to the lacustrine and full-marine carbonate deposits.

The large variety of non-marine carbonates also represents a fundamental tool for multidisciplinary research regarding environmental reconstructions and their evolution on Earth. For instance, the study by Bertini et al. (2021) concerns the investigation and analysis of Middle Pleistocene speleothems and the opportunity to unravel palaeoenvironmental and palaeoclimate changes by studying the contained pollen assemblage recovered, allowing the reconstruction of their development as a response to global events including teleconnections active between the Mediterranean Sea and the Atlantic Ocean circulation.

In consideration of their dependence from climate and environmental conditions, non-marine carbonates also became exploitable proxies in monitoring recent human-induced variations of our world. As showed by Bastianini et al. (2021), sedimentology of anthropogenic carbonates will help understanding carbonate precipitation mechanisms, and consequently will aid both efforts to utilise anthropogenic alkaline wastes for carbon capture and for managing their environmental impacts.

Non-marine carbonates include all the features in terms of processes, depositional environments, facies and architecture to be considered a challenging and frontier research topic in future geology:

- their global distribution is limited with respect to marine deposits and often more restricted in the geological record when preserved;
- processes controlling their deposition are extremely complex, often involving the contemporaneous and interdependent activity of abiotic and biogenic, microbially induced and influenced factors;
- a coherent nomenclature and fabric description are still debated, based on many different classification schemes and proposals progressively advanced during previous decades;

All these aspects require dedicated and prolonged studies aimed at solving questions around definitions and key concepts, but also their link to ambient and climate conditions which underpin applications as past environment archives. Their role at anthropogenic sites, including potential carbon sequestration technology, and significance for exo-terrestrial geology provide new applications for this knowledge. If we can fully unlock the secrets contained within non-marine carbonates this will provide enormous perspectives in the framework of environmental sustainability and climate change, preservation of natural resources, protection of global ecosystems and our understanding of the history of life in our solar system and beyond.

For all these reasons, we believe that non-marine carbonates represent a growing research field and an exciting opportunity for enthusiastic and questioning geologists.

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Figure 1: (A) Sub-lacustrine spring pinnacles from alkaline Mono Lake (California, USA); scale is 2 m. (B) Cascade tufa from Sarikavak (TK); scale is 175 cm. (C) Travertine deposits from Pamukkale (TK); scale is 170 cm. (D) Speleothems and flowstones from Kaklık Cave (TK); hammer for scale. (E) Temporarily exposed microbial bioherms at Bridger Bay shoreline, Antelope Island, Great Salt Lake (Utah, USA); sedimentologists for scale. (F) Upper Jurassic rhizolite laminar calcrete (base at hammer edge) from Rochaforte (Portugal; courtesy of V.P. Wright; Wright & Azerêdo, 2006). (G) The Brook Bottom leachate deposit (Harpur Hill, Derbyshire, UK). Anthropocene carbonate deposit forming downstream of a legacy deposit of impure lime, left by historical industrial activity at the site (courtesy of Laura Bastianini); scale is about 10 m.

